SORPTION AND TRANSPORT OF ACIDIC PESTICIDES IN VARIABLE-CHARGE SOILS

BY

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This work is dedicated to many scientists who have worked hard to lay the foundations upon which we have built our knowledge of soil and environmental sciences.

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Current models for estimating sorption of acidic compounds as a function of pH are based on some assumptions that may be unfounded. In this study a model of acidic pesticide sorption in soils was developed, considering initially a combination of a strongly acidic pesticide and a variable-charge soil with high clay content.

At low pH levels where acidic pesticides exist largely in neutral form, the soil sorbed much more 2,4-D than at high pH levels, where the pesticide is mostly in anionic form. Sorption of the acidic form is expected to decrease with increasing pH because the net negative charge on the soil minerals increases and ion-pair formation effects appear to be negligible. Contribution of 2,4-D anionic-form sorption was small when compared with its overall sorption. Therefore, the further modeling work of this study did not take into account the contribution of ionic interactions and data sets used from the literature

were not restricted to variable-charge soils. Dissociation of 2,4-D was not sufficient to explain the variation in K_d as a function of pH. Accessibility of soil organic functional groups able to interact with the pesticide (conformational changes) as a function of organic matter dissociation was proposed to explain the observed differences in sorption.

Experimental 2,4-D sorption data adequately fit the model presented, which explained a majority of the variation observed in the experimental data set. The model also accurately estimated K_{oc} values for flumetsulam and sulfentrazone in several soils. Therefore, it is apparent that anionic-form sorption has been overstated, and the effect of organic matter dissociation due to pH changes has been overlooked in previous studies. In addition, incorporating the developed sorption model made possible the improvement of an existing pesticide transport model.

CHAPTER 1
INTRODUCTION

Environmental Aspects of Acidic Pesticide Sorption and Transport in Soils

Much work has been done on pesticide sorption by soils, which has had either an emphasis on agricultural purposes or environmental concerns. After the application of pesticides to a soil system, various physical, chemical, physico-chemical, and biological processes determine their behavior. The fate of a pesticide in the environment is governed by the retention (sorption), transformation (chemical and biological degradation), and transport (volatilization, leaching, and overland flow) processes, and interactions of these processes (Cheng, 1990; Scheunert, 1992a; Schnoor, 1992).

In addition to the variety of processes involved in determining pesticide fate, many factors can affect the kinetics of such processes. Differences in chemical structures and properties of pesticides, and in soil properties and conditions, can all affect these environmental processes. Climatic conditions, composition of soil microorganism populations, presence or absence of plants, location of the soil in the landscape, and soil management practices can also affect the eventual fate of a pesticide in the soil environment. Furthermore, the rate and amount of water movement through the soil profile have a major impact on pesticide movement.

An understanding of pesticide transport processes in soil is essential to solve a number of problems facing agricultural and environmental scientists (Davidson *et al.* 1980). The variety of pesticides used represents many different classes of organic chemicals. The types of interactions of these compounds with different soil components are enormous, with almost a third of the active ingredients in current use being ionizable (acidic, basic, and amphoteric) compounds.

There are many ionizable organic compounds that have been designated as priority pollutants by the U.S. Environmental Protection Agency (EPA) (Keith and Telliard, 1979). Many of the priority pollutants are commonly used, weakly acidic pesticides (Hermosin and Cornejo, 1993).

Acidic pesticides are those compounds which are capable of dissociating into anionic forms in water, within the expected soil/water environmental pH range. The ionized forms behave differently than nonionic pesticides, seriously limiting generalizations that apply only to nonpolar compounds (Hornsby *et al.* 1996). Much of the soil chemistry of acidic pesticides may depend on the proportion of anionic and neutral forms. Hartley and Graham-Bryce (1980) and Green and Karickoff (1990) have discussed the consequences of ionization with respect to pesticide environmental behavior.

Given the increased use of acidic pesticides, concern has risen as to the possibility of these compounds remaining in the topsoil and eventually reaching surface waters by runoff, or leaching into the subsoil and eventually reaching groundwater. Many acidic pesticides have been detected in surface and ground waters (Wauchope, 1978; Goodrich *et al.*, 1991).

It is difficult to mathematically describe pesticide transport through soils at the microscopic level, because of an inadequate understanding of how specific processes behave in complex soil-water systems. Conceptual process models, which are mathematical representations of the modeler's understanding of various processes governing pesticide transport in soils, are common in the literature. These models are generally designed to work at macroscopic scale and are established from existing physical, chemical, and biological processes characterized under controlled soil-water conditions (Davidson *et al.*, 1980).

Study Objectives

Several models for estimating the sorption of acidic compounds as a function of pH have been presented in the literature. However, sorption of neutral and anionic forms only by organic matter, sorption of anionic form mainly at high pH levels, sorption of ionized form following formation of a neutral ion pair, invariant sorption of neutral form with pH, and linear pH-dependent sorption of anionic form have been explicitly or implicitly assumed in different studies. Some of these assumptions cannot be supported based on current knowledge, or do not have enough evidence in the literature with respect to soil pesticide sorption and related issues. This is particularly true for sorption by acid, variably charged, tropical and subtropical soils. Previous studies have overvalued sorption of anionic forms, and the overall effect of organic matter dissociation due to pH changes has been overlooked or neglected.

The purpose of the present study was to model the sorption and transport of acidic pesticides in soils. Combination of a strongly acidic pesticide and a high-clay-content soil with predominantly variable-charge minerals was initially chosen as an extreme case study for sorption.

Sorption of acidic compounds is mainly driven by their dissociation. In this study it is hypothesized that the sorption and consequently the transport of acidic pesticides also depends upon variable charges and organic matter dissociation in soils. Development of a sorption model from the underlying theory, along with empirical evidence from experimental work and the literature, was undertaken. Improvement of an existing pesticide-transport model was intended by incorporating the developed sorption model.

CHAPTER 2
REVIEW OF LITERATURE

The main soil factors impacting pesticide movement as noted in the literature are organic carbon content, acidity and alkalinity (expressed as pH), texture and physical structure, mineralogy, and associated soil hydraulic properties. These factors influence pesticide half-life, soil sorption, and physical movement of the compounds through soils.

Pesticides interact in complex ways with soil components in determining persistence and mobility of organic chemicals in soils. Pesticide movement has been shown to be inversely proportional to the degree of sorption. Several researchers also have suggested that sorption processes tend to limit the biodegradation rate of organic pesticides and contaminants (Subba-Rao and Alexander, 1982; Heitkamp *et al.*, 1984; Ogram *et al.* (1985); Mihelcic and Luthy, 1988; Stevens *et al.*, 1990).

Therefore, sorption has a profound impact on pesticide spatial distribution, bioavailability, and persistence in the environment. Extensively mobile pesticides may move into deeper soil layers where microbiological activity is often lower than that in topsoil layers, and this may have important implications with respect to persistence of residues (Nicholls *et al.*, 1987).

Fontaine *et al.* (1991) reported that, in a series of unpublished laboratory degradation experiments, the degradation rate of flumetsulam was faster in soils with

lower sorption capacities than in soils with high sorption capacities. Sorption was greater in soils with lower pH and higher organic carbon content. Ogram *et al.* (1985) suggested that microbial degradation of 2,4-D occurred only in the solution phase, and not when the pesticide was sorbed.

The term sorption is used to include a variety of possible associations between chemicals and solid phases. Multiple mechanisms of sorption may be involved in the association of a particular chemical with a given heterogeneous system such as soil.

Extensive research has been conducted on sorption of organic chemicals, particularly pesticides. Several reviews on this topic have been published, including Bailey and White (1970), Helling *et al.* (1971), Hamaker and Thompson (1972), Weber (1972), Green (1974), Weed and Weber (1974), Farmer (1975), Calvet (1980), Karickhoff (1980), Kenega and Goring (1980), Rao and Davidson (1980), McCall *et al.* (1981), Rao *et al.* (1983), Brusseau and Rao (1989a), Calvet (1989), Chiou (1989), Harmon *et al.* (1989), and Pignatello (1989).

Various soil properties have been identified as affecting the mechanism and degree of pesticide sorption (Bailey and White, 1964; Harris and Warren, 1964; Talbert and Fletchall, 1965; Bailey and White, 1970; Burchill *et al.*, 1981; Mingelgrin and Gerstl, 1983). The predominance of nonionic organic-compound sorption on soil organic matter has been extensively documented (e.g., Walker and Crawford, 1968; Bailey and White, 1970; Rao *et al.*, 1983).

According to Graham-Bryce (1981), while soil organic matter appears to dominate the sorption of most nonionized pesticides, this cannot be assumed for ionic or highly polar compounds. Many pesticides are weak acids or bases, so one factor that can

have a particularly marked influence on the sorption of ionized pesticides is pH. This is because the extent of sorption can differ greatly for the ionic and neutral forms of such compounds.

The solvent of interest in pesticide-soil interactions is water, which is itself highly polar. Thus, the charge or polarity of a pesticide is pertinent not only to its interaction with minerals and organic matter, but also controls its interaction with water (i.e, its water solubility). As pointed out by Weber (1970), sorption of a pesticide from solution onto a solid is not simply a two-component system. Water competes for the surface, as do any solutes in the system. The complexity of the sorption process thus probably exceeds any devised theoretical description (Weed and Weber, 1974). Sorption is the net result of pesticide-water, pesticide-soil and water-soil interactions. The relative affinities of all components in the system should be considered rather than only single interactions (Green, 1974).

Differences in sorption, which occur with changes in soil factors such as solution pH, are sometimes attributed only to pesticide-surface interactions. In fact, these factors may also influence pesticide-water interactions that indirectly affect sorption (Green, 1974). This largely determines a compound's solubility in water and also the extent to which a pesticide can compete with water for sorption sites on soil particles.

Acidic pesticides occur predominately as either anions or neutral molecules, depending upon whether the soil solution pH is above or below the acid dissociation constant (pK_A) for the compound. Theoretically, anionic and neutral forms will be present in equal amounts when the pH is equal to the pK_A (Grey *et al.*, 1997). Hence, the pK_A value, which represents the strength of the tendency of a chemical to ionize, is essential

information. It indicates if and within what pH range an acidic pesticide is predominately anionic.

As noted by Weber (1972), acidic pesticides are sorbed to organic soil colloids and the sorption depends upon pH, being greater under acid conditions where the pesticides are sorbed in molecular form. Sorption probably occurs through hydrogen bonding or weak physical sorption. For instance, Grover (1968) found that reducing soil pH from 6.5 to 5.0 reduced the bioactivity of picloram, owing to increased binding of molecular forms by organic matter.

Soil sorption of pesticides can be the result of physical or chemical processes. According to Koskinen and Harper (1990), unlike for hydrophobic organic compounds, reactions that ionizable organic pesticides undergo at the solid-water interface are more chemical in nature than entropy-driven partitioning; these interactions include van der Waals' bonding, hydrogen bonding, dipole-dipole interactions, ion-exchange, covalent bonding, protonation, ligand exchange, cation bridging, and water bridging.

The hydrogen bonding (a form of charge-transfer), ligand exchange, and ion-exchange processes are more site-directed and associated with specific functional groups (Pignatello, 1989). For a given compound, sorption to soil may be related to a continuum of sorption mechanisms and sites (Koskinen and Harper, 1990).

Acidic pesticides have been reported to be repelled from negatively charged alumino-silicate minerals, and sorbed in low to moderate amounts by soil organic matter (Talbert *et al.*, 1970; Adams, 1972; Weber, 1972; Mercies and Foy, 1986) and by hydroxyoxides (Weber, 1972). Bioactivity of many acidic herbicides has been represented as inversely related to soil organic matter content (Schliebe *et al.*, 1965; Herr *et al.*, 1966;

Grover, 1968; Kratky and Warren, 1973; Weber *et al.*, 1974; Harrison *et al.*, 1976; Anderson, 1985; Anderson and Barrett, 1985).

The pH-dependence of sorption has been reported for many acidic pesticides, including bentazon (Abernathy and Wax, 1973; Grey *et al.*, 1996), chlorimuron (Goetz *et al.*, 1989), chlorsulfuron (Shea, 1986; Walker *et al.*, 1989), metsulfuron-methyl (Walker *et al.*, 1989), and picloram (Nearpass, 1976).

Abernathy and Wax (1973) concluded that bentazone was mobile if the soil pH was near neutral. The high mobility around neutral pH was attributed to the combined effects of relatively high water solubility and acidic characteristic of the compound. A cation exchange resin retained no bentazone, while the greatest sorption occurred on an anion resin between pH 5 and 7. Bentazone has a pK_A of 3.2; thus, it exists predominantly in anionic form under pH conditions near neutrality. Additionally, Grey *et al.* (1996) noted that bentazone sorption decreased as pH increased for U.S. Coastal Plain Ultisols.

Goetz *et al.* (1989) evaluated chlorimuron sorption and mobility in Ultisols and Inceptisols, with sorption being inversely related to soil pH. Chlorimuron is a weak acid with a pK_A of 4.2; therefore, anionic forms predominate in solution for most soils.

Shea (1986) studied chlorsulfuron dissociation and sorption on selected sorbents and soils, and noted that lowering the pH increased herbicide sorption. However, it was shown that chlorsulfuron, which has pK_A 3.8, was not sorbed by technical kaolinite at pH 4.7.

Walker *et al.* (1989) measured sorption and degradation rates of chlorsulfuron and metsulfuron-methyl in soils taken from different depths. Sorption of both herbicides was negatively correlated with soil pH and positively correlated with organic matter content. It

was suggested that soil pH was the dominant factor controlling sorption in most soils. Chlorsulfuron and metsulfuron-methyl have pKA values of 3.8 and 3.3, respectively; hence, only under very acid conditions will a significant proportion of these herbicides exist in nonionized form.

Nearpass (1976) studied the sorption of picloram by humic acids and humin. As noted, the pH-dependent sorption of picloram (pKA = 3.4) agreed with the concept that its sorption is largely that of uncharged molecules. Sorbate-dependent pH effect and sorbent-dependent effects were pointed out.

Sorption of amphoteric compounds has also been shown to be inversely related to soil pH in different studies with, for example, imazaquin (Liu and Weber, 1985; Goetz *et al.*, 1986; Renner *et al.*, 1988; Loux *et al.*, 1989; Stougaard *et al.*, 1990; Regitano *et al.*, 1997) and imazethapyr (Renner *et al.*, 1988; Loux *et al.*, 1989; Stouggard *et al.*, 1990). Amphoteric pesticides contain groups that protonate at low pH, resulting in cationic forms, and dissociate to anionic forms at high pH levels. In the common soil pH range, imazaquin and imazethapyr occur predominantly in anionic form. Bioactivity of imazaquin was shown to be inversely related to soil organic matter, and directly related to soil pH (Loux *et al.*, 1989; Stouggard *et al.*, 1990).

Sorption of molecular forms of pesticides through physical forces is probably the primary sorption mechanism; however, sorption of anionic forms also may occur with some minerals, which have anion-exchange properties. Although most soils have a net negative charge due to the relative abundance of negative charges on crystalline alumino-silicates and organic matter, some soils which are composed principally of amorphous

alumino-silicates or oxides (hydroxides, oxyhydroxides) of iron and aluminum may have a net positive charge at low pH (Green, 1974).

Sorption of organic acids to iron and aluminum oxides occurs by a surface ligand-exchange reaction, as suggested by Nagarajah *et al.* (1970), Parfitt *et al.* (1977), Kummert and Stumm (1980), Zeltner *et al.* (1986), McBride and Wesselink (1988), and Kung and McBride (1989). The extent of sorption varies with sorbate aqueous dissociation and sorbent surface charge, in response to pH changes.

As noted by Grey *et al.* (1997), sorption of anionic forms of pesticides by weathered soil is largely dependent on soil components with pH-dependent charges, such as kaolinite and hydroxyoxides of iron and aluminum, including, gibbsite, goethite, and hematite (Hingston *et al.*, 1972; Albro *et al.*, 1984; Allen and Hajek, 1982; McBride, 1989; Schulze, 1989). These minerals have pH-dependent charges and become positively charged at low pH values (Tisdale *et al.*, 1985).

The pH value resulting in charge neutrality is referred to as the point of zero charge (PZC), and varies with the specific mineral in question (Parks and de Bruyn, 1962; Parks, 1965; Parks, 1967; Hingston *et al.*, 1972; van Raij and Peech, 1972; Uehara and Gillman, 1981). Kaolinite can develop a net positive charge when pH drops below 6.7 (Bohn *et al.*, 1985; Harper, 1994). The PZC values of iron and aluminum hydroxides are between 8.5 and 10.4 (McBride, 1989). Therefore, these minerals are sorptive to anions, provided that pH is below the PZC.

Hingston *et al.* (1972) reported that decreasing soil pH resulted in increased inorganic anion sorption for soils that were rich in goethite and gibbsite. The decrease in cation exchange capacity (CEC) and increase in anion exchange capacity (AEC) with

decreased pH is typical of highly weathered soils in which the minerals are principally kaolinite and oxides. The pH-dependent nature of surface charge on kaolinite and oxides is noteworthy from a practical point of view, in that soil pH is one property that is commonly altered during soil management.

Goetz *et al.* (1986) found iron and aluminum hydroxides (specifically hematite and gibbsite) and kaolinite to be the predominant soil components controlling sorption of imazaquin when organic carbon content was low (<1%) and at pH values where imazaquin exists almost exclusively as an anion. Imazaquin is an amphoteric compound which contains an acidic carboxyl group with dissociation constant of 3.8, and a basic quinoline group with dissociation constant of 2.0. Hydroxyoxides have also been implicated in the sorption of acidic herbicides such as picloram (Hammaker *et al.*, 1966) and 2,4,5-T (O'Connor and Anderson, 1974).

Enhanced partitioning of organic ions by ion pairing with inorganic counterions in solution has been shown for octanol-water systems (Westall *et al.*, 1985; Jafvert, 1990; Johnson and Westall, 1990) and hypothesized for soil-water systems (Jafvert, 1990; Lee *et al.*, 1990). As noted by Westall *et al.* (1985), ion-pair formation is favored at high salt concentration.

Regitano *et al.* (1997) investigated the role of inorganic cations in solution on the sorption of imazaquin. Similarity in the relationship observed between data from different electrolyte solutions suggested that differences in sorption resulted primarily from changes in soil solution pH.

In addition, the influence of inorganic anions present in solution was investigated by Regitano *et al.* (1997). The authors suggested that the phosphoric acid ion ($H_2PO_4^-$)

competes with imazaquin for sorption sites or radically modifies the nature of sorbing surface sites. The inhibition may be due to competition between ions for anion-exchange sites or other specific sites of sorption (Barrow, 1989). Nearpass (1976) found little competition between picloram (an acidic herbicide) and phosphate ions when using humin and humic acid as sorbents. Thus, Regitano *et al.* (1997) suggested that, if phosphate competition occurs, it is most likely at mineral surface sites.

Nearpass (1976) observed an increase in picloram sorption by humin and humic acids at pH values close to the compound's pK_A (3.4), when a small change in pH with increasing ionic strength would result in a significant increase in the neutral fraction of the herbicide. Higher ionic strengths result in displacement of more hydrogen ions from soil solids, thereby reducing soil solution pH and shifting acidic compounds towards neutral forms.

Regitano *et al.* (1997) also assessed the influence of electrolyte ionic strength on imazaquin sorption. Overall, variations observed between solutions with different ionic strengths appeared to be small. However, enhanced sorption with increasing ionic strength was observed for soils where pH-induced changes in dissociation were negligible.

As pointed out by Calvet (1989), an aspect of the evaluation of sorption is the need to estimate the environmental fate of chemicals. Since site-specific experimental characterization of sorption is time consuming and demands well-equipped laboratories, several relationships have been proposed to approximate sorption coefficients.

Bailey *et al.* (1968) early noted the difficulty in predicting sorptive behavior for pesticides that dissociate to form an ion. Several factors, such as dissociation, soil

solution pH, ionic strength and composition, and surface charge, may have to be considered to successfully predict sorption of acidic compounds by soils. Furthermore, sorption of ionizable organic compounds can occur through various mechanisms (Koskinen and Harper, 1990).

Jafvert (1990) presented a method to obtain sorption coefficients for organic acid compounds by sediments. Invariant sorption of neutral form with pH and linear pH-dependent sorption of anionic form were assumed. Fontaine *et al.* (1991) obtained anionic and neutral sorption coefficients using nonlinear optimization of flumetsulam sorption normalized with respect to organic carbon, as a function of pH. Sorption of neutral and anionic forms was assumed to occur only on organic matter.

Lee *et al.* (1990) showed that equilibrium sorption of pentachlorophenol (PCP) could be predicted from a knowledge of soil solution pH, organic carbon content, and pK_A value of PCP. Regitano *et al.* (1997) combined the data on imazaquin sorption obtained in their study with a data set from Loux *et al.* (1989). The model presented by Lee *et al.* (1990) was fitted to the combined data to optimize for values of organic-carbon-normalized coefficients, with sorption of anionic form being much lower than that observed for molecular form.

According to Regitano *et al.* (1997), reasonable agreement between that model and measured data implied that pH determined in the bulk soil solution is representative of pH encountered by the herbicide at the sorbent surface. It also implied that the majority of sorption observed for imazaquin can be explained by assuming that sorption is primarily to soil organic carbon, where the contributions of sorption in neutral and anionic forms are additive. Although predictions from the model were generally

satisfactory, extreme deviations observed for some soils suggest that sorption of imazaquin may also be influenced by nonhydrophobic interactions with organic matter or mineral surfaces (Loux *et al.*, 1989).

CHAPTER 3
THEORETICAL MODELING OF ACIDIC PESTICIDE SORPTION BY VARIABLE-CHARGE SOILS

The primary soil properties affecting pesticide sorptivity are variable, depending on the specific compound. One generalization that appears to hold in the literature is that the single most important soil property affecting pesticide sorption is soil organic carbon content. Nonhydrophobic interactions, however, may contribute to sorption under some conditions. This appears to occur with highly polar or ionizable compounds, and is more apparent for soils with low organic carbon content and high clay content.

As noted by Pignatello (1989), many researchers have recognized that the organic fraction of soils dominates the sorption of nonionic compounds at organic carbon levels of more than 0.1%, whereas below this value interactions with mineral surfaces may be more important. According to Karickhoff (1984), for a ratio of mineral to organic carbon fractions less than 30 (w:w), mineral contributions to sorption are expected to be masked, regardless of mineral content. This is in accordance with the hypothesis of mineral blockage by organic matter (Walker and Crawford, 1968), and is associated with the concept of sorbent availability.

General Sorption Model

The general term sorption is used to indicate a process by which pesticides are partitioned between the dissolved and sorbed phases. Many times it is difficult to fully distinguish between the mechanisms of physical and chemical sorption processes. If pesticide sorption is treated as an instantaneous, reversible, and linear process, the sorbed phase concentration (S) in soils can be related to the dissolved phase concentration (C) by the following:

$$S = K_d \cdot C \qquad [3\text{-}1]$$

The coefficient K_d is known as the distribution or sorption coefficient, which is equal to the slope of the linear sorption isotherm. This coefficient is a function of properties of soil and pesticide. Linear sorption isotherms have been shown to apply reasonably well at low concentrations for nonionic organic compounds (Karickhoff *et al.*, 1979).

Acidic Pesticides as Sorbates

As noted previously, some effort has also been devoted to understanding the sorption of organic acidic compounds for modeling purposes. Jafvert (1990) presented a method to obtain sorption coefficients of organic acid compounds on sediments. In the model developed, invariant sorption of neutral form with pH and linear pH-dependent

sorption of anionic form were assumed. Anionic form sorption was considered to occur mainly at high pH levels, whereas sediments, as well as soils, are expected to be negatively charged.

Lee *et al.* (1990) showed that equilibrium sorption of organic acidic compounds could be predicted with a knowledge of soil solution pH, soil organic carbon content, and the compound's pK_A value. Sorption by soils at any pH was predicted by a weighted combination of sorption coefficients for neutral molecule and organic anion normalized to soil organic carbon content.

Fontaine *et al.* (1991) obtained anionic and neutral sorption coefficients as best-fit parameters using nonlinear optimization of sorption for an acidic herbicide normalized by organic carbon content for 21 different soils, as a function of pH. Sorption of neutral and anionic forms was assumed to occur solely on organic matter.

For ionizable compounds, Equation 3-1 can be expressed as

$$S = (K'_m \cdot C_m) + (K'_i \cdot C_i) + (K'_{ip} \cdot C_{ip}) + E \qquad [3\text{-}2]$$

where K' is the prime sorption coefficient, *m* denotes the compound in molecular form, *i* denotes the free-ion form, *ip* denotes any ion-pairs, and the E term represents the error.

This model can be thought of as comprised of a deterministic part (the first three terms) and a stochastic part (E). The most frequent general assumption about the error term is that it is independently and identically normally distributed with a constant but unknown variance (Ratkowsky, 1990).

Equation 3-2 can be rewritten as the following:

$$S = \Sigma\,(K'_z \cdot C_z) + E \qquad [3\text{-}3]$$

where z denotes the pesticide's form (molecule, free-ion, or ion-pair) and C_z represents the concentration of each fraction of pesticide form.

Equation 3-2 can also be expressed as

$$S = (K'_m \cdot \phi_m + K'_i \cdot \phi_i + K'_{ip} \cdot \phi_{ip})\, C + E \qquad [3\text{-}4]$$

in which ϕ is the fraction of pesticide form and C stands for total pesticide concentration.

Equation 3-4, in turn, can be rewritten as

$$S = \Sigma\,(K'_z \cdot \phi_z \cdot C) + E \qquad [3\text{-}5]$$

where the product $(K'_z \,.\, \phi_z)$ is the sorption coefficient for each pesticide form (K_z), and K'_z is the prime sorption coefficient for the respective pesticide-form fraction.

Particularly for acidic compounds, the fractions of molecular and anionic forms can be estimated, respectively, by

$$\phi_m = (1 + 10^{\,pH - pK_A})^{-1} \qquad [3\text{-}6]$$

and

$$\phi_a = 1 - \phi_m \qquad [3\text{-}7]$$

where pK_A stands for the dissociation constant of a given acidic compound, and *m* and *a* denote the molecular (neutral) and anionic pesticide forms, respectively.

According to Hornsby *et al.* (1996), the acid ionization (or dissociation) constant can be defined starting with the molecular (neutral) form of a pesticide. Losing a proton produces an anionic form of the pesticide, and the equilibrium reaction can be expressed as

$$XH = X^- + H^+ \qquad [3\text{-}8]$$

in which XH, X^-, and H^+ represent the molecular acidic pesticide, the anionic form, and the hydrogen ion, respectively.

Thus, the equilibrium constant (K_A) is defined as

$$K_A = \frac{[X^-]\cdot[H^+]}{[XH]} \qquad [3\text{-}9]$$

where brackets indicate solution equilibrium concentrations.

This approach should prove adequate at typical concentrations of pesticides in the environment (Hornsby *et al.,* 1996), and the acid dissociation constant (pK_A) can be expressed as the following:

$$pK_A = -\log_{10}(K_A) \qquad [3\text{-}10]$$

Therefore, the larger the value for the pK_A of a pesticide, the weaker the acid and, thus, the less the tendency for Reaction 3-8 to go to the right. Ion-pair complexes can form in solution or at the soil-solution interface, with the formation of ion-pairs favored primarily at high complementary-ion concentrations (Westall *et al.*, 1985). No consistent evidence of the general relevance of ion pairing for ionizable pesticides in soils has been found in the literature. However, whether or not ion-pair formation is considered, ionic pesticide forms will partially combine with counter ions in solution, resulting in neutral or at least less-charged forms.

Among the several parameters that can affect pesticide sorption are the composition and ionic strength of the electrolyte solution. For the ionic strength range of interest, the sorption coefficient of nonionic compounds should increase no more than a factor of 1.2 and, therefore, ionic strength effects should be minor according to Karickhoff (1984).

For soils as a sorbent mixture, the concentration of sorbed pesticide can be taken as a weighted-average sum over all components:

$$S = \Sigma\,(K'_{x,z} \cdot F_x \cdot \phi_z \cdot C) + E \qquad [3\text{-}11]$$

in which F stands for the respective soil component fraction and x denotes the soil components (e.g., various mineral forms and organic carbon).

In short, pesticide sorptivity (δ) is a function of the ratio between sorbed (denoted by *s*) and solution (denoted by *w*) phase affinities (a):

$$\delta \int\left(\frac{as}{aw}\right) \qquad [3\text{-}12]$$

This is consistent with the fugacity concept described by Makay (1979) for environmental systems and by Karickhoff (1984) with emphasis on organic pollutant sorption in aquatic systems. The prime sorption coefficient (K') can also be expressed as a product of a reference coefficient (κ) and a variable component (γ):

$$K' = \kappa \cdot \gamma \qquad [3\text{-}13]$$

The coefficient κ refers to the magnitude of the sorption coefficient, and is a theoretical value, which is not expected to vary largely. On the other hand, the variable γ changes with different soil conditions including pH levels. Changes in the pH of a soil system can alter both pesticide-surface affinity and pesticide-water affinity.

<u>Variable-Charge Minerals as Sorbents</u>

In weathered soils with variably charged minerals, such as kaolinite, iron and aluminum oxides, the variable term (γ in Equation 3-13) for ionic forms of pesticides is expected to be primarily pH-dependent. These soils are characterized by surfaces having a

constant surface potential, and the surface charge varies with changes in electrolyte concentration and in activity of the potential-determining ions, H^+ and OH^-. Thus, changes in pH lead to variation in mineral surface charges. For colloids with a reversible interface, the surface potential at any given pH should be independent of electrolyte concentration. For this reason, such interfaces are characterized by a constant surface potential. With the potential remaining constant, the surface charge changes with varying electrolyte concentration (van Olphen, 1963; van Raij and Peech, 1972; Uehara and Gillman, 1981).

The surface electric potential (ψ_o) due to charges is determined by the soil solution pH and is given by a Nernst-type relation:

$$\psi_o = \left(\frac{R \cdot T}{F}\right) \cdot \ln\left\{\frac{(H^+)}{(H_o{}^+)}\right\} \qquad [3\text{-}14]$$

where R represents the gas constant, T is the absolute temperature, F represents the Faraday constant, and (H^+) and $(H_o{}^+)$ stand for hydrogen ion activity in solution at a given pH and at the soil's point of zero charge (PZC), respectively. The PZC is the pH value at which the net surface charge reduces to zero (Parks and de Bruyn, 1962).

Net surface charge (σ) can be related to the surface potential by a direct relationship given by the Gouy-Chapman theory of the diffuse double layer for a symmetric electrolyte. According to van Raij and Peech (1972), Gouy-Chapman theory is not adequate to describe realistically the relation between surface charge and surface potential at high values for the latter.

In the Stern theory (Adamson, 1967), surface charge is assumed to be balanced by the charge in solution which is distributed between two layers. The charge in the layer closer to the surface (sorbed ions), called the Stern or compact layer, is represented by σ_1. The charge in the second layer of ions (the diffuse layer) is represented by σ_2.

Therefore, the net surface charge (σ) in both layers is simply the summation of charges in the Stern layer and the diffuse layer ($\sigma_1 + \sigma_2$). The charge in the Stern layer (σ_1) is given by

$$\sigma_1 = \frac{N \cdot z \cdot e}{1 + (\frac{A \cdot \rho}{M \cdot \eta}) \cdot \exp(-\frac{z \cdot e \cdot \psi_d + \phi}{k \cdot T})} \qquad [3\text{-}15]$$

in which N stands for the number of available sorption sites per cm^2 of surface, z is the counter-ion valence, e is the electron charge, A is Avogadro's number, ρ represents the density of water, M is the molecular weight of water, η is the electrolyte concentration, ψ_d refers to the potential at the boundary between the Stern layer and the diffuse layer (the Stern potential), ϕ accounts for the energy of specific sorption for counter ions by the surface, and k represents the Boltzman constant.

The charge in the diffuse layer (σ_2) is given by Gouy-Chapman theory; however, the reference now is the Stern potential (ψ_d) instead of the surface potential (ψ_o):

$$\sigma_2 = (\frac{2\eta \cdot \varepsilon \cdot k \cdot T}{\pi})^{1/2} \cdot \sinh(\frac{z \cdot e \cdot \psi_d}{2k \cdot T}) \qquad [3\text{-}16]$$

where ε is the dielectric constant of water.

The net surface charge is also given by the equation:

$$\sigma = \left(\frac{\varepsilon'}{4\pi \cdot \delta}\right) \cdot (\psi_o - \psi_d) \qquad [3\text{-}17]$$

where ε' is the average dielectric "constant" in the medium of the Stern layer and δ is the thickness of the Stern layer.

As noted by van Raij and Peech (1972), some of the problems inherent in the Stern theory arise from the fact that N, ε', and δ are not known. Nevertheless, it is possible to calculate the net surface charge by introducing reasonable values for these parameters, which can be adjusted according to experimental observations. Thus, the double layer potential at any pH value can be calculated if PZC is known.

In general, it can be said that the PZC reflects the overall composition of a system. For soil systems, if it is assumed that mineral and organic components act independently and do not influence each other's behavior, the PZC will reflect the weight-averaged sum of their organic and inorganic constituents. The presence of iron and aluminum oxides will tend to increase the PZC toward higher pH values, whereas the presence of clay minerals with permanent or structural negative charge and of organic matter will shift the PZC to lower pH values (Parks, 1965; Parks, 1967). For instance, the PZC can be as high as about 6 for the extreme case of the acric B-horizon of some Oxisols, with large amounts of iron and aluminum oxides and low organic matter contents (Casagrande *et al.*, 1999).

Soil Organic Matter as a Sorbent

As noted by Stevenson (1982), Senesi (1992), and Almendros (1995), the mechanisms involved in organic-solute sorption into or onto soil organic matter have not been clearly demonstrated. Soil organic matter is a complex and heterogeneous mixture of primarily humic substances, polysaccharides, lignin, simple carbohydrates, lipids, proteins, and organic acids (Stevenson, 1982; Hayes, 1985). Organic matter can also be associated with alumino-silicates, iron and aluminum hydroxides, and other inorganic constituents in soil.

It is known that soil organic matter properties affect the sorption of organic molecules (Wershaw, 1986), which involves several mechanisms (Stevenson, 1982; Almendros, 1995). Several hypotheses on the structure of organic matter have been proposed (Allison, 1968; Schnitzer and Khan, 1978; Stevenson, 1982). During the formation of organic matter, differences in structure and characteristics may arise as a function of local conditions. Rearrangements and reactions within the organic matter structure also continue after its formation in soils (Stevenson, 1982; Haider, 1992).

Soil organic matter, in fact, is very complicated though most models that consider organic matter as a sorbent assume that its structure is simple. In equilibrium approaches, organic matter has been treated as a phase that behaves like an organic solvent (Chiou, 1989). Organic matter has also been conceptualized as an organic polymer through which the solute diffuses to sorption sites (Brusseau and Rao, 1989b).

Humic and fulvic acids and humin are often employed as model soil organic matter fractions. According to Nearpass (1976), since humin is insoluble in both alkali

and acid, it can be postulated as the foundation material to which humic and fulvic acids and other extractable materials are bonded. The humic and fulvic acids can be considered to exhibit pH-dependent bonding to the humin fraction and, therefore, the humin fraction of soil organic matter may be a stronger sorptive site for nonionized molecules than either humic or fulvic acid.

The organic-carbon-normalized sorption coefficient (K_{oc}) measured for the same organic molecule may vary considerably among different soils (Scheunert, 1992b). This suggests that sorption studies should consider, among other factors, the influence of soil physico-chemical conditions (i.e., pH and ionic strength) on polarity and accessibility of different organic matter functional groups (Stevenson, 1982; Schnitzer, 1991; Senesi, 1992).

Either in soils with variably or "permanently" charged minerals, the sorption coefficient can vary due to organic matter dissociation, even for pesticides in neutral form. Based on what was noted by Nearpass (1976), that humin seems to be a material to which the humic and fulvic acids are bonded, organic matter dissociation may unblock sites that then become suitable for pesticide sorption.

As pH rises, the degree of negative charge increases because of the deprotonation or dissociation of H^+ from functional groups in organic matter. As noted by Bohn *et al.* (1985), the dissociation of carboxyl and phenol groups yields perhaps 85 to 90% of the negative charge of soil organic matter. Cross-linked molecular chains constitute the basic framework of soil organic matter. Stretching among the branched chains has been attributed to enhanced repulsive forces through ionization.

Soil organic matter becomes more soluble at higher pH as dissociation increases the surface negative charge of the organic particles (McBride, 1994). Intermolecular and intramolecular electrostatic repulsion is believed to be responsible for this increased solubility, although other forces are probably important as well. The repulsive forces cause an unfolding and expansion that are associated with dispersion and dissolution of organics, and hence humin becomes more accessible for solute sorption. At low pH values organic matter is in flocculated form instead (McBride, 1994) and, thus, the soil organic functional groups able to interact with solutes are less accessible.

The complex and heterogeneous soil organic acids have several functional groups with different pK_A values, and more than one acidic group on each molecule. According to Sparks (1995), carboxyl is a major acidic functional group which has a dissociation constant, expressed as pK_A, less than 5, while Bohn *et al.* (1985) reported that many carboxylic groups are sufficiently acid to dissociate below pH 6. Thus, dissociation constant (pK_A) values close to 5 for whole organic matter are expected.

As noted by McBride (1994), an array of equilibrium functions has been developed to characterize the acid-base behavior of synthetic and natural polyelectrolytes. The most common is the extended Henderson-Hasselbach equation:

$$pH = pK_A + n \cdot \log\{\frac{\alpha}{(1-\alpha)}\} \qquad [3\text{-}18]$$

where α is defined as the degree of dissociation of the acidic functional groups, and pK_A and n are empirical constants for a given titration. In addition to indicating the pH at

which half-neutralization occurs ($\alpha = 0.5$), the dissociation constant (pK_A) also provides a rough guide to the expected degree of ionization at higher and lower pH levels. As noted by Stevenson (1982), humic substances undoubtedly deviate from this general rule, but perhaps only slightly so.

It is noteworthy that the pK_A term in the Henderson-Hasselbach equation is defined as the "apparent pK_A ", and is not a true acid dissociation constant. As well as pK_A, the *n* parameter can be varied to fit the titration curves of organic matter to Equation 3-18. According to McBride (1994), when this is done, the value of *n* is usually found to be about 2. The *n* parameter is related to inclination of the dissociation curve and has been included because soil organic matter has many functional groups with different pK_A values.

Rearranging Equation 3-18, an expression for organic matter dissociation can be written as follows:

$$\left\{\frac{\alpha}{(1-\alpha)}\right\} = 10^{(\frac{1}{n})\cdot(pH - pK_{om})} \qquad [3\text{-}19]$$

where pK_{om} stands for the apparent acid dissociation constant of organic matter.

Sorption Model for Acidic Pesticides in Variable-Charge Soils

As noted previously, acidic pesticides can exist in different proportions of neutral and anionic forms in soils, depending upon the pH level (Equations 3-6 and 3-7). In

variable-charge soils, particle surface charges also change with pH, and positive net charges can occur. Thereby, in addition to sorption of neutral pesticide forms, anionic forms can sorb on positively charged minerals to some degree, and large pH effects can be expected.

Ignoring ion-pairing, Equation 3-5 for acidic pesticides in soils with variable-charge minerals can be written as follows:

$$S = (K'_m \cdot \phi_m \cdot C) + (K'_a \cdot \phi_a \cdot C) + E \qquad [3\text{-}20]$$

or

$$S = (K'_{oc,m} \cdot F_{oc} \cdot \phi_m \cdot C) + (K'_{min,a} \cdot F_{min} \cdot \phi_a \cdot C) + E \qquad [3\text{-}21]$$

where oc and min refer to, respectively, soil organic carbon and minerals, assuming no sorption of the pesticide in anionic form on organic matter and in molecular form on minerals.

The organic-carbon-normalized prime sorption coefficient of molecular form ($K'_{oc,m}$), accordingly to Equation 3-13, can be expressed as the following:

$$K'_{oc,m} = (\kappa'^{d}_{oc} \cdot f^{d}) + (\kappa'^{n}_{oc} \cdot f^{n}) \qquad [3\text{-}22]$$

where f^d and f^n are estimates of the fractions of organic carbon (dissociated and nondissociated, respectively) and are related to the accessibility of soil organic functional

groups able to interact with solutes (humin) as a function of organic matter dissociation. Thus, $\kappa'_{oc}{}^{d}$ and $\kappa'_{oc}{}^{n}$ are the reference prime sorption coefficients of molecular form of the pesticide normalized for organic carbon in, respectively, dissociated and nondissociated forms of organic matter.

From Equation 3-19, the accessibility of humin in dissociated and nondissociated organic matter (f^d and f^n, respectively) can be estimated as

$$f^{d} = \frac{10^{(\frac{1}{n})\cdot(pH-pKom)}}{1+10^{(\frac{1}{n})\cdot(pH-pKom)}} \qquad [3\text{-}23]$$

and

$$f^{n} = 1 - f^{d} \qquad [3\text{-}24]$$

It is worth noting that the molecular form of pesticides, even though neutral, can still exhibit polarity to different degrees. Therefore, $\kappa'_{oc}{}^{d}$ and $\kappa'_{oc}{}^{n}$ values also depend on polar characteristics of the molecular form of each compound.

Based on Equation 3-13, the mineral-normalized prime sorption coefficient of anionic form ($K'_{min,a}$) can be expressed as follows:

$$K'_{min,a} = (\kappa'_{min}{}^{+} \cdot f^{+}) \qquad [3\text{-}25]$$

in which f^+ is the estimate of fraction of the minerals positively charged. Thus, $\kappa'_{min}{}^+$ refers to the reference prime sorption coefficient of the anionic form normalized for positively charged soil minerals.

CHAPTER 4
MODELING pH EFFECTS ON SOIL SORPTION OF ACIDIC PESTICIDES

Sorption coefficients for neutral and anionic forms, based on traditional interpretation of batch equilibrium experiments, are empirically combined to produce an overall sorption coefficient. In this chapter the theoretical modeling presented previously is combined with experimentally determined and published sorption coefficient data. It is intended to offer a model based on current understanding of the contribution of nonionic and ionic processes to the sorption of acidic pesticides, with emphasis on weathered, variable-charge soils.

The herbicide 2,4-D was chosen as a model acidic pesticide, which can exist in molecular and anionic forms in soils. In fact, due to its low pK_A value (2.8), 2,4-D appears predominately in anionic form in the pH range common to variable-charge soils. Hence, ionic sorption also can occur on positively charged soil minerals.

The herbicide 2,4-D has been used for many years and remains one of the most widely applied herbicides in the world today. The U.S. Environmental Protection Agency (EPA) considers it a priority pollutant (Keith and Telliard, 1979; Hermosin and Cornejo, 1993). Much early work was conducted on the interaction between 2,4-D and clay minerals or soil organic matter (e.g., Weber *et al.*, 1965; Norris and Greiner, 1967; Haque and Sexton, 1968).

There have been many research studies of pesticide sorption mechanisms on isolated soil fractions. However, as pointed out by Graham-Bryce (1981), mostly due to the heterogeneity of the surfaces which makes results very difficult to interpret, there has been less work on mechanisms of sorption by whole soils. As noted by Karickhoff (1984), although highly elegant in many respects, studies of pesticide-clay mineral interactions are largely irrelevant to modeling purposes. In such studies, the mineral surfaces are highly prepared while, in natural systems, mineral surfaces are commonly covered with coatings (organic and inorganic polyelectrolytes).

Weathered soils with variable-charge minerals constitute an important soil category in tropical and subtropical agricultural regions of the world (e.g., Brazil, Australia, India, China, Central Africa, the U.S. southeastern region and Hawaii). Oxisols are highly weathered soils containing kaolinite and iron and aluminum oxides. According to Huang *et al.* (1977), hydroxy-iron and -aluminum soil compounds exhibit a high sorption capacity for phenolic acids (such as 2,4-D), which is attributed to the large chemical reactivity of these positively charged minerals towards the negatively charged carboxyl and phenolic hydroxyl groups of the phenolic acid compounds.

Materials and Methods

Samples of an Oxisol were collected in Ribeirão Preto region, São Paulo State, Brazil, and soil properties were determined according to methods presented by EMBRAPA (1979) and Camargo *et al.* (1986). Thus, clay content was determined based on a method presented by Bouyoucos (1927) and texture was classified according to the

USDA system (USDA, 1975), while mineralogy description was based on methods presented by Jackson (1969). The point of zero charge (PZC) was determined based on the method of van Raij and Peech (1972). The method used for organic carbon (OC) determination was that of Walkley and Black (1934). Soil pH was measured in 1:1 (w:w) soil and 0.01 M calcium chloride ($CaCl_2$) solution mixtures. Soil properties are presented in Table 4-1. This Oxisol was chosen due to its high clay content and predominance of variable-charge (amphoteric) minerals.

Table 4-1. Properties of the soil used in the 2,4-D sorption experiment.

Clay Content (%)	Organic Carbon (%)	CEC[1] (cmol/kg)	$pHCaCl_2$	PZC	Mineralogy[2]
64	1.6	10.3	4.9	4.1	K>Gi>>H≈Go

Typic Haplorthox (USDA, 1975), Rhodic Ferralsol (FAO, 1971), Latossolo Roxo (EMBRAPA, 1988). [1] Cation exchange capacity at pH 7. [2]K = kaolinite, Gi = gibbsite, H = hematite, Go = goethite.

In a sub-sample, soil pH changes were promoted by addition of 1 *M* hydrochloric acid, HCl, or 1 *M* calcium hydroxide, $Ca(OH)_2$, to produce values either below or above its natural pH level. Soil samples were moistened to field capacity and allowed to equilibrate for 6 weeks. Each soil sample was re-moistened to field capacity every 2 days.

Another set of soil sub-samples was used to study the effects of organic matter removal from the soil on sorption, at different pH levels. Soil was treated with hydrogen

peroxide (H_2O_2) based on methods presented by Jackson (1958) and Black (1965), and the residual organic carbon content was measured. Then, pH changes were also carried out as described above.

Sorption coefficients were determined using a standard batch equilibrium method, with 10 mg of analytical 2,4-D [C.A. name: (2,4-dichlorophenoxy) acetic acid; CAS RN: 94-75-7] per liter of a 0.01 *M* $CaCl_2$ solution being used. A 10 mL aliquot of the solution was added to 5 g of soil in a centrifuge tube, and it was shaken in an agitator for 24 h. at about 25°C. Previous studies have shown that more than 90% of the 2,4-D sorption occurs within 2 h.

At the end of the equilibrium period, the suspensions were centrifuged for 20 min at 10,000 rpm, and the supernatant filtered through a 0.45 μm filter. The amount of pesticide in the supernatant was determined by high performance liquid chromatography (HPLC) analysis (column: C_{18} Waters NovaPak, 3.9 by 150 mm, 5 μm particle diameter), with duplicate injections of supernatant and standard solutions being made. The mobile phase was methanol/water 70:30 (v:v) and 0.01 *M* tetrabutyl-ammonium chloride, with detection being performed at 228 nm. Supernatant pH values were read on a pH meter, and changes in pesticide sorption with pH were studied.

Sorption at equilibrium was calculated as the difference in concentration between the initial solution and solution at equilibrium with the soil. Previous studies have shown that the 2,4-D isotherms for several soils have an approximately linear form; therefore, sorption was measured at a single solution concentration for each pH level, and an apparent K_d value was calculated. Thus, the overall sorption coefficient (K_d) was

calculated as $K_d = S / C$, where S is the mass of sorbed herbicide per mass of soil (μg/g) and C is the herbicide concentration of the supernatant solution at equilibrium (μg/mL).

In addition, soil sorption data for other acidic pesticides, covering a large range of pK_A values, were collected from the literature. Fitness of the theoretical model to the measured and collected sorption data sets was evaluated using the SAS/STAT program (SAS, 1989). The NLIN procedure in SAS fits nonlinear regression models using a least squares method. A Gauss-Newton procedure was used for finding the least squares estimator (Bard, 1974; Kennedy and Gentle, 1980; Draper and Smith, 1981). Based on Myers (1986), an F-test was applied and the coefficient of determination (R^2) was calculated for a given nonlinear model.

From Equation 3-20, omitting the error term (E), the overall sorption coefficient (K_d) can be expressed as:

$$K_d = (K'_m \cdot \phi_m) + (K'_a \cdot \phi_a) \qquad [4\text{-}1]$$

where $(K'_m \cdot \phi_m)$ represents the sorption coefficient of pesticide in molecular form (K_m), and $(K'_a \cdot \phi_a)$ is the sorption coefficient of pesticide anionic form (K_a) on positively charged soil particles.

The prime sorption coefficient of pesticide in molecular form (K'_m) is, in fact, a composite coefficient and depends on effects of organic matter dissociation on the accessibility of humin, which can be estimated using Equations 3-23 and 3-24. In turn, values for the prime sorption coefficient of pesticide in anionic form (K'_a) are a function of positive charges on soil minerals (or a function of soil positive net charge). The net

charge can be estimated using Equations 3-14 through 3-17, and by introducing reasonable values for required parameters, which can be adjusted according to experimental observations. Thus, it should be possible to calculate the double layer potential at any pH value as the point of zero net charge (PZC) is known.

Finally, Equation 4-1 can be rewritten as:

$$K_d = (K'_{oc,m} \cdot F_{oc} \cdot \phi_m) + (K'_{min,a} \cdot F_{min} \cdot \phi_a) \qquad [4\text{-}2]$$

where $K'_{oc,m}$ is the organic-carbon-normalized prime sorption coefficient of molecular form, F_{oc} is the soil organic carbon fraction, ϕ_m is the fraction of pesticide in molecular form, $K'_{min,a}$ is the mineral-normalized prime sorption coefficient of anionic form, F_{min} is the soil mineral fraction, and ϕ_a is the fraction of pesticide in anionic form.

Results and Discussion

The results from sorption studies are presented in Table 4-2 and shown in Figure 4-1. Changes in sorption coefficient values measured for whole soil (i.e., without organic matter removal) can be seen as a function of pH. At low pH, where acidic pesticides exist largely in neutral form, the soil sorbs much more 2,4-D as compared to sorption at high pH, where the pesticide is mostly in anionic form. Therefore, it is suggested that the anionic form of 2,4-D has much lower sorption coefficient than the neutral form.

Ionic interactions may contribute, to some degree, to anionic pesticide sorption under some conditions. As noted by Karickhoff (1984), this is more apparent in soils

with low organic carbon content and high clay content. Based on the hypothesis of mineral blockage by organic matter, mineral contribution is expected to be at a maximum when the ratio of mineral to organic carbon fractions is more than 30, regardless of the mineral content.

Table 4-2. Sorption coefficient (K_d) values of 2,4-D, at different pH levels, measured for whole soil (Typic Haplorthox) and when organic matter was removed.

pH(1)	K_d (mL/g)	
	Soil(2)	Soil – OM(3)
2.5	27.9	1.9
3.2	23.4	NA
3.5	18.6	2.3
4.0	7.8	1.1
4.7	2.7	0.5
4.9	2.1	NA
5.6	1.1	0.1
6.2	0.4	NA

(1)Supernatant pH. (2)Whole soil (1.6% OC). (3)Soil after organic matter removal (0.1% OC). NA = data not available.

Changes in sorption coefficients measured when organic matter was removed can also be seen as a function of pH in Table 4-2 and Figure 4-1. The curve for the whole soil refers to the overall sorption coefficient (K_d), and the curve for the soil with organic matter removed can be related approximately to the anionic sorption coefficient (K_a).

However, the removal of soil organic matter by H_2O_2 treatment is not complete. In this study, the organic carbon content was reduced to 0.1% after treatment. Therefore, some residual organic matter content remains in the soil, still covers mineral surfaces, and contributes to (or controls) pesticide sorption.

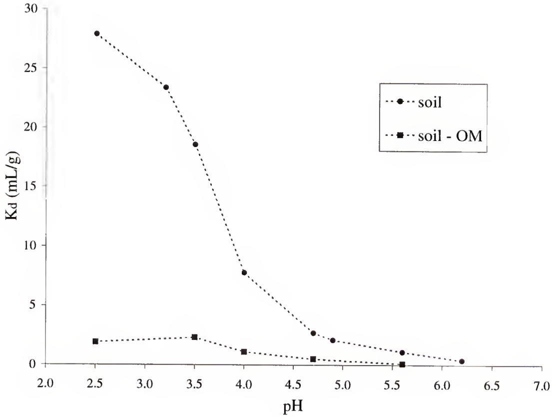

Figure 4-1. Sorption coefficients of 2,4-D measured for whole soil (Typic Haplorthox) and when organic matter was removed, as a function of pH.

Many researchers have recognized that, at organic carbon levels below 0.1%, interactions of nonionic organic compounds with mineral surfaces may be more important (Pignatello, 1989). However, that would be an unrealistically low organic matter content for Oxisols such as that used in the present study under natural conditions, even in the B_w horizon.

According to Stevenson (1982), clay and organic matter function more as a unit than as separate entities, and the relative contributions of organic and inorganic surfaces to sorption depend upon the extent to which the clay is coated with organic substances. The whole soil used here had a mineral to organic carbon ratio of 40 and, when organic matter was removed, that ratio increased drastically and, consequently, the soil PZC rose. Therefore, the maximum contribution of mineral ionic sorption was expected after organic matter removal.

However, when organic matter was removed, the sorption of 2,4-D diminished markedly (Table 4-2 and Figure 4-1). As a consequence of organic matter removal, sorption at different pH levels was about ten-fold smaller than sorption for the whole soil. This seems to parallel approximately the reduction in soil organic carbon content. Thus, interaction of organic matter with minerals still provides an organic surface for sorption.

The anionic form of the pesticide, owing to its relative larger size and lower concentration, is not able to compete effectively for anion exchange sites with other anions present in the soil solution. On the other hand, ion pairing between the pesticide's anionic form and cations in the soil solution could occur, and sorption of neutral ion-pairs would be possible. This process depends on cation (complementary-ion) availability in solution, either due to high salt concentrations (Westall *et al.*, 1985) or near negatively charged colloidal surfaces.

It is known that sorption of 2,4-D is mainly driven by its dissociation; however, 2,4-D dissociation is not enough to explain the variation in K_d as a function of pH. Assuming that the overall K_d is dominated by sorption of the molecular form, the prime

sorption coefficient of the pesticide, estimated by the expression $K'_m = K_d / \phi_m$ using data presented in Table 4-2, increases markedly when pH values rise as shown in Figure 4-2.

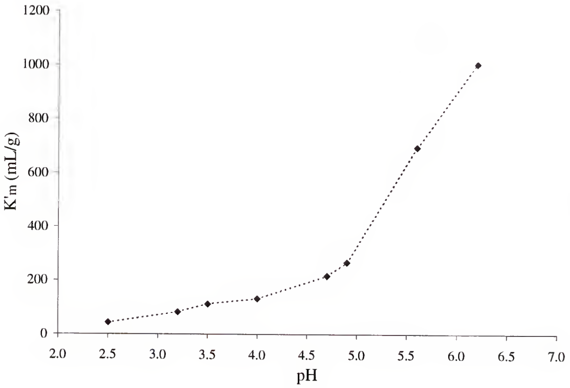

Figure 4-2. Prime sorption coefficient of 2,4-D, as a function of pH, when assuming that the overall K_d is dominated by sorption of the molecular form.

Concurrently, as noted in a previous section, organic matter becomes more accessible for solute sorption at high pH due to conformational changes. Therefore, accessibility of organic matter functional groups able to interact with the pesticide may explain some of the differences observed in sorption coefficient values. Furthermore, hydrophobicity of the neutral form of the pesticide, expressed as K'_m, does not appear to vary substantially at low pH levels (Figure 4-2), and it is apparent that protonation of organic matter at very low pH does not necessarily make it more hydrophobic.

Previous efforts to model sorption of acidic organic compounds have, in general, overvalued anionic-form sorption. On the other hand, the overall effect of organic matter dissociation owing to pH changes has been overlooked. Jafvert (1990), Lee *et al.* (1990), and Fontaine *et al.* (1991) tried to explain greater sorption than would be expected for acidic compounds, particularly at high pH levels.

Jafvert (1990) presented a model assuming invariant sorption of the neutral form with pH and linear pH-dependent sorption of the anionic form. Anionic-form sorption was considered to occur mainly at high pH. However, based on current knowledge sorption of anionic form would not be expected, owing to the predominant negative surface charge in sediments, as well as in soils, at high pH levels. His modeling work was based on a sediment with 49.4% clay content and 1.5% organic carbon; therefore, most of the mineral surfaces were expected to be covered by organic matter.

Fontaine *et al.* (1991) obtained anionic and neutral sorption coefficients using nonlinear optimization of sorption normalized by organic carbon as a function of soil pH. Sorption of neutral and anionic forms was assumed to be occurring only on organic matter. However, anionic-form sorption is not expected on organic matter, except at very low pH levels, when some functional groups become positively charged (e.g., amines).

As pointed out by Bohn *et al.* (1985), soil organic matter possessing a net positive charge has not been found at normal soil pH values. Protonated amide groups may yield positive charge mostly at very low pH levels; in spite of this, the overall charge on organic matter remains negative.

Lee *et al.* (1990) showed that equilibrium sorption could be predicted using a weighted combination of sorption coefficients for the neutral molecule and organic anion,

normalized to soil organic carbon content. The assumption was made that sorption of the ionized form may occur upon formation of a neutral ion-pair. It was also suggested that the hydrophobic part of the organic anion might sorb to a hydrophobic surface, with its polar end oriented toward the more polar aqueous phase. However, if these processes truly occur, they might not be relevant because it has been shown that overall sorption of acidic compounds decreases markedly with pH when the anionic form is dominant.

Further work to model the variable component (γ) in Equation 3-13 for ionic interactions as a function of pH was not pursued in this study due to the small contribution of anionic sorption when compared with overall sorption (Figure 4-1). This was even true in this specific case, which involves a combination of an acidic pesticide with low pK_A (strong acid) and a soil with high clay content and predominantly variable-charge minerals (kaolinite, gibbsite, hematite, and goethite).

Therefore, recalling Equation 3-22, Equation 4-2 can be written as:

$$K_d = \{(\kappa'^{d}_{oc} \cdot f^{d}) + (\kappa'^{n}_{oc} \cdot f^{n})\} \cdot F_{oc} \cdot \phi_m \qquad [4\text{-}3]$$

or

$$K_{oc} = \{(\kappa'^{d}_{oc} \cdot f^{d}) + (\kappa'^{n}_{oc} \cdot f^{n})\} \cdot \phi_m \qquad [4\text{-}4]$$

where ϕ_m, f^d, and f^n are estimated with Equations 3-6, 3-23, and 3-24, respectively. The values of the empirical constant, n, and the apparent dissociation constant for organic matter, pK_{om}, used in this study (Equation 3-23) were in accordance with expected values

reported by McBride (1994), that is n = 2, and Bohn *et al.* (1985) and Sparks (1995), pK_{om} = 5. As noted previously in Chapter 3, κ'^{d}_{oc} and κ'^{n}_{oc} coefficients are reference values for the magnitude of sorption, while the estimates of the accessibility of humin in dissociated and nondissociated organic matter (f^d and f^n) are expected to change with pH. They, along with ϕ_m, will define the shape of the K_d vs. pH curve.

Fitness of the theoretical model in Equation 4-4 to the measured 2,4-D sorption data set for the whole soil was evaluated. The measured data and fitted curve using the NLIN procedure of the SAS/STAT program (SAS, 1989) are presented in Figure 4-3, and the estimated values for κ'^{n}_{oc} and κ'^{d}_{oc} were 0.49 x 10^3 mL/g and 41.03 x 10^3 mL/g, respectively.

The F-test shows that pH significantly (at 1% level of the F-distribution) influences the values of overall organic-carbon-normalized sorption coefficient (K_{oc}). The experimental data fit the model (Equation 4-4) adequately. The coefficient of determination (R^2), which is a measure of the fit, shows that the model is able to explain 99.3% of the variation observed in the experimental data set (Figure 4-3).

The analysis made here should be applicable for other compounds as well, for verifying if the model represents good fit to the response of sorption as a function of pH. Thus, searching for expressions of Equation 4-4 for other acidic pesticides, K_d data from the literature were collected and curves were fitted following the same methodology. The contribution of ionic interactions to sorption of 2,4-D was shown to be much smaller than nonionic contributions. Henceforth, the data sets presented in this study will not be restricted to variable-charge soils.

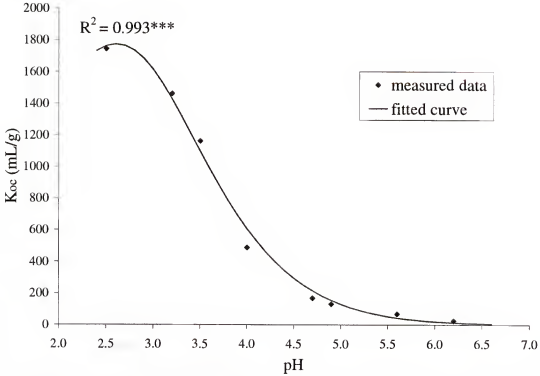

Figure 4-3. Measured data and fitted curve when using Equation 4-4 for pH-dependence of 2,4-D sorption (pKA = 2.8), expressed by K_{oc}, for whole soil (Typic Haplorthox).

Fontaine *et al.* (1991) reported K_{oc} data for flumetsulam [C.A. name: N-(2,6-difluorophenyl)-5-methyl [1,2,4] triazolo [1,5-a] pyrimidine-2-sulfonamide; CAS RN: 98967-40-9] in soils adjusted to different pH levels. Flumetsulam (a sulfonamide herbicide) is weakly acidic, with pKA of 4.6. The measured data and fitted curve according to Equation 4-4 are presented in Figure 4-4. Though fit for the individual soils was excellent, use of the entire data set to fit an overall curve was less satisfactory but still highly significant with R^2 of 0.660.

The values of κ'^{n}_{oc} and κ'^{d}_{oc} for flumetsulam are reported in Table 4-3, including the overall values resulting from fitting all original K_{oc} values for several pH levels in all soils. Sorption was measured on four soils with adjusted solution pH values. The soils

used were a Typic Argiudoll (Soil 1), a Typic Hapludult (Soil 2), a Udic Haploboroll (Soil 3), and a Typic Haplaquoll (Soil 4), and soil properties are presented in Table A-1 (Appendix).

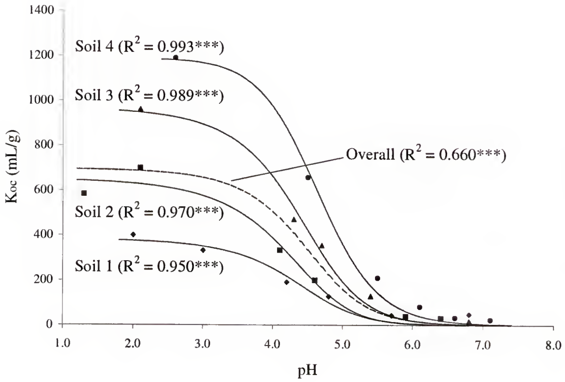

Figure 4-4. Measured K_{oc} data set from Fontaine *et al.* (1991), and fitted curves when using Equation 4-4 for flumetsulam (pK_A = 4.6) in four different soils.

Grey *et al.* (1997) reported K_d values for sulfentrazone {C.A. name: N-[2,4-dichloro-5-[4-(difluromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl] phenyl] methanesulfonamide; CAS NR: 122836-35-5} for four soils with different amended pH values. The soils were a Typic Unifluvent (Soil 1), a Rhodic Paleudult (Soil 2), an Aeric Ochraqualf (Soil 3), and a Typic Rhodudult (Soil 4). Soil properties are presented in Table A-2 (Appendix). The clay fraction was determined to be predominantly comprised

of kaolinite for Soils 1 and 2, equal amounts of kaolinite and smectite were found in Soil 3, and Soil 4 contained a combination of kaolinite and iron and aluminum oxyhydroxides of hematite and gibbsite. Sulfentrazone (phenyl-triazolinone herbicide) is a weak acid with pK_A of 6.6.

The calculated K_{oc} values and fitted curve using Equation 4-4 for sulfentrazone are shown in Figure 4-5, and the values of $\kappa'_{oc}{}^{n}$ and $\kappa'_{oc}{}^{d}$ are presented in Table 4-4. Use of the entire data set to fit an overall curve still produced a highly significant R^2 of 0.748.

Table 4-3. Values of reference prime sorption coefficients normalized for nondissociated and dissociated organic carbon fractions ($\kappa'_{oc}{}^{n}$ and $\kappa'_{oc}{}^{d}$, respectively) for flumetsulam.

Soil	$\kappa'_{oc}{}^{n}$ (10^3 mL/g)	$\kappa'_{oc}{}^{d}$ (10^3 mL/g)
Soil 1	0.38	0.10
Soil 2	0.65	0.04
Soil 3	0.97	0.38
Soil 4	1.18	1.33
Overall$^{(1)}$	0.70	0.43

$^{(1)}$Resulting from fitting all original K_{oc} values for several pH levels in all soils to Equation 4-4. Source of collected data: Fontaine *et al.* (1991).

The model presented here was able to estimate K_{oc} values for 2,4-D, flumetsulam, and sulfentrazone as a function of pH in several soils. However, it is apparent from

Figures 4-4 and 4-5 that variability of the measured K_{oc} data between different soils increases when pH decreases, especially for pH levels below the pesticide pK_A values.

The high variability (highly scattered points) in K_{oc} values could be attributed to the fact that the soil organic matter is mostly in nondissociated form at low pH levels. In other words, at low pH values, organic matter is in flocculated form and, therefore, the pesticide has to diffuse to sorption sites through organic matter strands (Brusseau and Rao, 1989b). The humin fraction of soil organic matter seems to offer a stronger sorptive site for nonionized molecules than humic and fulvic acid. Humin can be considered the foundation material to which humic and fulvic acids are bonded (Nearpass, 1976).

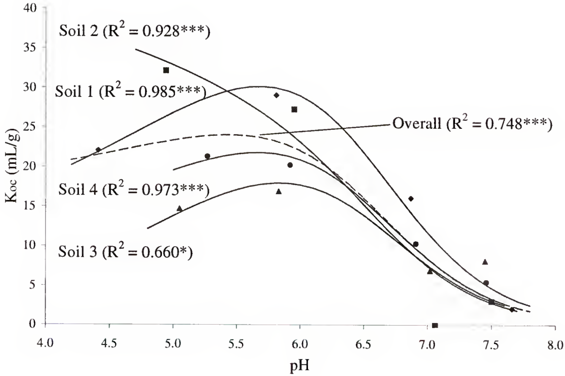

Figure 4-5. Calculated K_{oc} data set from Grey *et al.* (1997), and fitted curves when using Equation 4-4 for sulfentrazone (pK_A = 6.6) in four different soils.

Differences in structure and composition of soil organic matter may arise as a function of local conditions (Stevenson, 1982; Haider, 1992). Thus, hydrophobic sorption depends on the variable physical structure and composition of the solid-phase organic matter, especially at low pH levels. It has to be kept in mind that acidic compounds are predominantly in neutral form at pH levels below their pKA values.

Table 4-4. Values of reference prime sorption coefficients normalized for nondissociated and dissociated organic carbon fractions ($\kappa'_{oc}{}^{n}$ and $\kappa'_{oc}{}^{d}$, respectively) for sulfentrazone.

Soil	$\kappa'_{oc}{}^{n}$ (10^3 mL/g)	$\kappa'_{oc}{}^{d}$ (10^3 mL/g)
Soil 1	0.01	0.04
Soil 2	0.04	0.02
Soil 3	0.01	0.03
Soil 4	0.01	0.03
Overall[(1)]	0.02	0.03

[(1)]Resulting from fitting all original K_{oc} values for several pH levels in all soils to Equation 4-4. Source of collected data: Grey *et al.* (1997).

In fact, it is difficult to distinguish between two-dimensional sorption onto the soil organic matter surface and sorption within the actual three-dimensional polymeric structure of organic matter (Graham-Bryce, 1981). General (non-specific) processes can explain apparent pesticide affinity for organic matter. However, as noted by Graham-Bryce (1981), it should be emphasized that, for the system being considered, there are

three main components: water, pesticide, and surface. The relative strengths of attractions of these different components for themselves and for each other determine the resultant equilibrium distribution.

CHAPTER 5
LEACHING POTENTIAL ASSESSMENT FOR ACIDIC PESTICIDES

Because of an inadequate understanding of how specific processes behave in complex soil-water systems, it is difficult to describe mathematically pesticide transport through soils at the microscopic level. Therefore, macroscopic and conceptual-process models are common in the literature (Davidson *et al.*, 1980).

Several authors have proposed screening methods for determining whether a pesticide is likely to leach. Some have attempted to set threshold values for a physical property or set of properties which, when exceeded, should indicate that the pesticide will leach. Others have presented simple analytical or numerical models which are run using measured or estimated properties of pesticide and soil, in order to predict the likelihood of leaching.

A number of comprehensive computer simulation models are available for site-specific evaluations of pesticide behavior in the root zone. Models have also been developed to describe various environmental processes that influence pesticide dynamics in soils. Such models are usually data-intensive and require knowledge of a number of soil environment, crop, and pesticide parameters. In a majority of the cases, such parameters are neither available nor likely to be available in the near future because of the

high cost associated with obtaining such data for a large number of soil-crop-pesticide combinations.

Experience has shown that the response of complex natural systems can often be represented by models of low order and few parameters that incorporate the dominant modes of behavior (DeCoursey, 1992). For many years, pesticide mobility has been identified as a key characteristic when assessing leaching potential. It has led to use of such factors as soil thin-layer chromatography residence time, octanol-water partition coefficient, and pesticide distribution or organic-carbon partition coefficient to rank the potential for chemical mobility in soil.

However, mobility alone is not a good indicator of leaching and groundwater contamination potential. Rather, the combination of mobility and persistence determine whether or not a compound will be degraded to an innocuous form or to an insignificant concentration during its residence time in the vadose zone.

As an alternative to simple mobility indices, Jury *et al.* (1983) recommended use of a screening model that includes the influence of mobility and biochemical half-life in assessing the potential for leaching. A similar approach was used by Rao *et al.* (1985) in forming a simple index based on vadose-zone residence time in the soil and biochemical half-life.

Jury *et al.* (1983) defined the convective time as a function of soil bulk density, fraction of organic carbon, organic-carbon pesticide partitioning coefficient, volumetric water content, volumetric air content, Henry's law constant for partitioning between the aqueous and vapor phases, distance over which flow occurs, and water flux. Only

advective transport of pesticides was considered, and piston flow of water in soil was assumed, along with instantaneous equilibrium between sorbed and solution phases.

In comparisons where soil bulk density, fraction of organic carbon, and relation between distance over which flow occurs and water flux are held relatively constant, organic-carbon pesticide partitioning coefficient (K_{oc}) has been shown to be a useful index of mobility or predictor of advective time. Compounds with low K_{oc} have smaller advective time and, therefore, are more likely to move over greater distances or in a shorter time and to have a higher potential to leach.

Rao *et al.* (1985) incorporated pesticide degradation functions into expressions for travel time to yield the Attenuation Factor (AF) model, which is the relation between pesticide mass entering groundwater at some distance below the soil surface and pesticide mass applied to the surface. In computing relative mobility indices, Jury *et al.* (1984) used an arbitrary depth of 10 cm, while Rao *et al.* (1985) used the approximate actual distance to groundwater underlying a given soil in computing the relative leaching potential.

In reality, flow through the root zone is highly transient, and the degradation rates are probably different in the two zones. This may be important in situations where a chemical is rapidly flushed to the vadose zone by rainfall shortly after chemical application. Once in the vadose zone the degradation rate may be lower than in the root zone, so that potential transport to groundwater may be significantly underestimated. However, these assumptions may not present a serious problem when developing a relative ranking of compounds if it is realized that the relative position or rank may change somewhat under different assumptions about soils and climatic patterns.

The purpose of this study was to estimate the sorption and transport (mobility) of acidic pesticides in soils, comparing the original and modified AF models for multi-layered soils. The original AF model was modified by introducing the concept of pH-dependence for K_d, and using the equations developed and parameters estimated in Chapter 4. The original and modified models, considering soil and pesticide properties, were applied to assess the leaching potential of selected pesticides in several Brazilian soils.

Materials and Methods

Leaching potentials of three acidic pesticides (2,4-D, flumetsulam, and sulfentrazone) were assessed for several soils of the Ribeirão Preto region, State of São Paulo, Brazil. Pesticide properties are presented in Table 5-1. Soil samples were obtained from the Espraiado watershed, and their properties were determined based on methods presented by EMBRAPA (1979), and Camargo *et al.* (1986). A total soil depth of 120 cm was considered, and soil parameters used in this study are presented in Tables 5-2, 5-3, and 5-4. These properties represent those of major soils in that region. The net recharge rate (50 cm/yr.) in the watershed was estimated as the difference between rainfall (150 cm/yr.) and evapotranspiration (100 cm/yr.). This assumes steady flow in the soil zone considered.

The Espraiado watershed is located in an area where the risks of contamination tend to be high for groundwater because of aquifer vulnerability (Spadotto, 1996; Spadotto *et al.*, 1998; Gomes, 1998). The watershed is on a recharge area of an important

aquifer which covers about 1,194,000 km^2 and is one of the world's largest (Rebouças, 1994; Araújo *et al.*, 1995).

The highly weathered Oxisols, with large areas in Brazil and other parts of the world, present very stable aggregates coated with oxides and organic matter, and the hydraulic conductivity of many clayey Oxisols is considerable (Sanchez, 1976). Oxisols have variable charge because of the presence of pH-dependent minerals such as kaolinite, and iron and aluminum hydroxides, as well as due to organic matter. The Quartzipsamments are sandy soils with low organic matter content and high hydraulic conductivity.

Table 5-1. Properties of selected acidic pesticides.

Pesticide	Dissociation Constant pK_A [1]	Sorption Coefficient			Half-life
		K_{oc} [1, 2] (mL/g)	K_{oc}^{n} [3] (10^3 mL/g)	K_{oc}^{d} [3] (10^3 mL/g)	$t_{1/2}$ [1, 4] (days)
2,4-D	2.8	20	0.49	41.03	10
Flumetsulam	4.6	35	0.70	0.43	60
Sulfentrazone	6.6	10	0.02	0.03	200

[1]Data from literature (Jury *et al.*, 1984; Rao *et al.*, 1985; Fontaine *et al.*, 1991; Hornsby *et al.*, 1996; Grey *et al.*, 1997; Tomlin, 1997), and databases (PIPs/EXTOXNET; PPD/ARS/USDA). [2]Average K_{oc} value at pH 6 - 7, considering no pH-dependence. [3]Overall value estimated by using Equation 4-4; [4]Considering that $t_{1/2}$ does not depend on sorption.

Table 5-2. Properties of Soil 1 (Quartzipsammentic Haplorthox).

Depth (cm)	$pHCaCl_2$	Clay (%)	Porosity (%)	Field Capacity (%)	Bulk Density (g/cm^3)	Organic Carbon (%)
0-20	5.1	24	55.8	22.3	1.29	0.72
20-40	4.9	26	62.1	21.7	1.22	0.50
40-60	4.8	30	54.9	21.3	1.21	0.34
60-80	4.6	29	54.4	20.2	1.28	0.25
80-100	4.4	32	56.5	19.6	1.21	0.22
100-120	4.1	34	51.7	18.8	1.16	0.20

Table 5-3. Properties of Soil 2 (Typic Haplorthox).

Depth (cm)	$pHCaCl_2$	Clay (%)	Porosity (%)	Field Capacity (%)	Bulk Density (g/cm^3)	Organic Carbon (%)
0-20	5.3	68	58.2	26.2	1.37	1.38
20-40	5.1	74	57.7	24.6	1.38	1.05
40-60	4.9	73	60.4	23.5	1.32	0.87
60-80	4.8	70	61.6	23.1	1.19	0.67
80-100	4.6	67	65.2	22.8	1.16	0.64
100-120	4.2	63	64.7	21.4	1.18	0.60

Table 5-4. Properties of Soil 3 (Typic Quartzipsamment).

Depth (cm)	$pHCaCl_2$	Clay (%)	Porosity (%)	Field Capacity (%)	Bulk Density (g/cm^3)	Organic Carbon (%)
0-20	5.3	6	44.6	19.4	1.46	0.30
20-40	5.2	8	62.5	18.7	1.52	0.24
40-60	5.0	11	61.0	17.3	1.48	0.20
60-80	4.8	8	42.3	17.0	1.46	0.13
80-100	4.5	7	57.6	16.5	1.45	0.08
100-120	4.2	10	61.7	16.1	1.44	0.03

Leaching potentials of the pesticides were assessed for multi-layered soils by means of the AF model, as presented by Rao *et al.* (1985) and Hornsby and Rao (1998). According to Rao *et al.* (1985), AF is defined as the fraction of the amount of pesticide applied at the soil surface that leaches through a given soil depth. It is expressed as the following:

$$\mathrm{AF} = \exp(-t_r \cdot k) \qquad [5\text{-}1]$$

where *tr* is the travel time and *k* is the first-order rate constant for pesticide degradation.

Pesticide half-life ($t\frac{1}{2}$) is related to k by

$$k = \frac{0.693}{t\frac{1}{2}} \qquad [5\text{-}2]$$

and the travel time is defined as follows:

$$tr = (\mathrm{L} \cdot \mathrm{RF} \cdot \frac{\mathrm{FC}}{q}) \qquad [5\text{-}3]$$

where L represents the distance to groundwater, FC is the soil field capacity, and q stands for the net recharge rate. The retardation factor (RF) for pesticide flow is

$$\mathrm{RF} = 1 + \frac{(\mathrm{BD} \cdot \mathrm{F_{oc}} \cdot \mathrm{K_{oc}})}{\mathrm{FC}} + \mathrm{AC} \cdot \frac{\mathrm{K_H}}{\mathrm{FC}} \qquad [5\text{-}4]$$

where BD stands for the soil bulk density, F_{oc} is the fraction of organic carbon, K_{oc} is the organic-carbon pesticide sorption coefficient, AC is the air-filled porosity, and K_H represents the dimensionless form of the Henry's law constant. The organic-carbon-normalized sorption coefficient (K_{oc}) is defined as

$$\mathrm{K_{oc}} = \frac{\mathrm{K_d}}{\mathrm{F_{oc}}} \qquad [5\text{-}5]$$

where K_d is the pesticide sorption coefficient. For pesticides with low volatility (i.e., low K_H values), retardation factor can be simplified to

$$RF = 1 + \frac{(BD \cdot F_{oc} \cdot K_{oc})}{FC} \quad [5\text{-}6]$$

In a post-publication addendum, Hornsby and Rao (1998) presented a generalized form of Equation 5-1 for a multi-layered soil as follows:

$$AF = \Pi \exp(-tr_i \cdot k_i) \quad [5\text{-}7]$$

in which Π stands for the product of the expression $\exp(-tr_i \cdot k_i)$ over all layers, and the subscript i designates the ith layer; thus, $i = 1,..., n$, where n represents the number of layers, and the values for tr and k are unique to each layer.

Thus, AF was also calculated for each pesticide using the modified model. Equation 4-4 and parameters that were estimated in Chapter 4 were introduced to calculate K_d values as a function of pH.

Results and Discussion

Pesticide sorption coefficient (K_d) values were calculated from literature data and estimated by Equation 4-4 for 2,4-D, flumetsulam, and sulfentrazone in different layers of each soil. Results are presented in Tables 5-5, 5-6, and 5-7.

The pH-dependent K_d values estimated for all three pesticides were always higher than pH-independent K_d values calculated using average K_{oc} data. The K_d values, as expected, were the lowest for Soil 3, and highest for Soil 2. Soil 3 has the lowest organic carbon (OC) content, while Soil 2 has the highest OC content.

Table 5-5. Sorption coefficient values calculated from literature data (K_d) and estimated using Equation 4-4 (K_d*) for 2,4-D in different layers of Soil 1 (Quartzipsammentic Haplorthox), Soil 2 (Typic Haplorthox), and Soil 3 (Typic Quartzipsamment).

Depth (cm)	Soil 1		Soil 2		Soil 3	
	K_d (mL/g)	K_d* (mL/g)	K_d (mL/g)	K_d* (mL/g)	K_d (mL/g)	K_d* (mL/g)
0-20	0.14	0.79	0.28	1.05	0.06	0.23
20-40	0.10	0.77	0.21	1.15	0.05	0.22
40-60	0.07	0.62	0.17	1.34	0.04	0.26
60-80	0.05	0.63	0.13	1.22	0.03	0.24
80-100	0.04	0.76	0.13	1.61	0.02	0.24
100-120	0.04	0.06	0.12	2.76	0.01	0.14

It is worth noting that the pH-independent K_d values follow primarily the decrease of OC with depth. The pH-dependent K_d values for the three pesticides evidenced a large variation from layer to layer following changes in OC and pH for the different soil depths. That is, K_d depends on a combined effect of these two soil parameters. When OC decreases, K_d tends to decrease; on the other hand, lowering pH tends to increase K_d.

For all three soils, OC and pH exhibit an overall decrease with depth. However, for Soils 1 and 2, OC contents do not vary largely below 60 cm; thus, decreases in pH result in increasing K_d values for 2,4-D and flumetsulam (Tables 5-5 and 5-6, respectively). For Soil 3, OC content continues to decrease with depth below 60 cm, and 2,4-D and flumetsulam K_d values drop concurrently.

Table 5-6. Sorption coefficient values calculated from literature data (K_d) and estimated using Equation 4-4 (K_d*) for flumetsulam in different layers of Soil 1 (Quartzipsammentic Haplorthox), Soil 2 (Typic Haplorthox), and Soil 3 (Typic Quartzipsamment).

Depth (cm)	Soil 1		Soil 2		Soil 3	
	K_d (mL/g)	K_d* (mL/g)	K_d (mL/g)	K_d* (mL/g)	K_d (mL/g)	K_d* (mL/g)
0-20	0.25	0.96	0.48	1.24	0.10	0.27
20-40	0.17	0.96	0.37	1.41	0.08	0.26
40-60	0.12	0.76	0.30	1.66	0.07	0.32
60-80	0.09	0.74	0.23	1.50	0.04	0.29
80-100	0.08	0.82	0.22	1.91	0.03	0.27
100-120	0.07	0.96	0.21	2.67	0.01	0.13

The pH effect on sulfentrazone sorption is shown to be very interesting. Because of its high pK_A value (6.6), sulfentrazone K_d reaches a "maximum" value at higher pH values when compared with 2,4-D and flumetsulam (Figures 4-1 through 4-4). Thus,

sulfentrazone K_d values do not increase when pH drops below 60 cm in all three soils (Table 5-7).

Table 5-7. Sorption coefficient values calculated from literature data (K_d) and estimated using Equation 4-4 (K_d*) for sulfentrazone in different layers of Soil 1 (Quartzipsammentic Haplorthox), Soil 2 (Typic Haplorthox), and Soil 3 (Typic Quartzipsamment).

Depth (cm)	Soil 1		Soil 2		Soil 3	
	K_d (mL/g)	K_d* (mL/g)	K_d (mL/g)	K_d* (mL/g)	K_d (mL/g)	K_d* (mL/g)
0-20	0.07	0.18	0.14	0.34	0.03	0.07
20-40	0.05	0.12	0.10	0.26	0.02	0.06
40-60	0.03	0.08	0.09	0.21	0.02	0.05
60-80	0.02	0.06	0.07	0.16	0.01	0.03
80-100	0.02	0.05	0.06	0.15	0.01	0.02
100-120	0.02	0.04	0.06	0.14	0.00	0.01

The AF was also calculated for different layers of each soil. These results are presented in Figures 5-1, 5-2, and 5-3, where AF is expressed as percentage of pesticide mass applied at soil surface. Overall AF values for each soil are presented in Figure 5-4. Despite differences between the pH-independent Kd and the pH-dependent Kd values, the AF values for 2,4-D, calculated by the original model and by the modified model, were similarly low for all three soils (Figures 5-1). The low AF values are mostly due to the short half-life of 2,4-D.

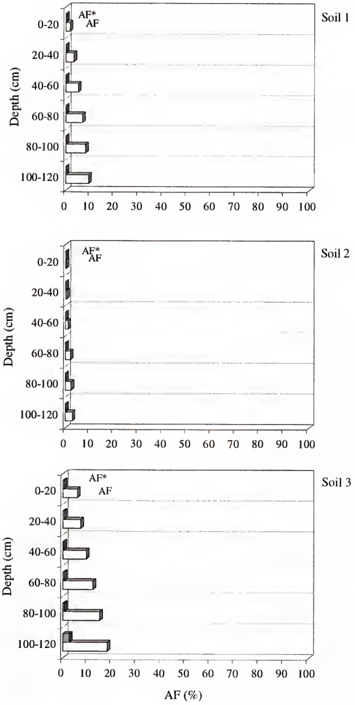

Figure 5-1. Attenuation factor values calculated using literature-based K_d data (AF) and estimated K_d data (AF*) for 2,4-D in different layers of Soil 1 (Quartzipsammentic Haplorthox), Soil 2 (Typic Haplorthox), and Soil 3 (Typic Quartzipsamment).

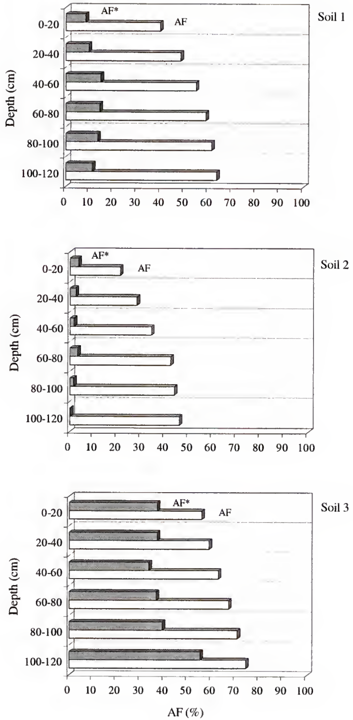

Figure 5-2. Attenuation factor values calculated using literature-based K_d data (AF) and estimated K_d data (AF*) for flumetsulam in different layers of Soil 1 (Quartzipsammentic Haplorthox), Soil 2 (Typic Haplorthox), and Soil 3 (Typic Quartzipsamment).

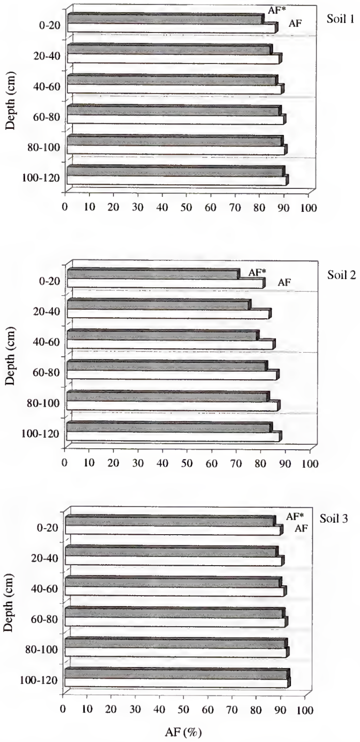

Figure 5-3. Attenuation factor values calculated using literature-based K_d data (AF) and estimated K_d data (AF*) for sulfentrazone in different layers of Soil 1 (Quartzipsammentic Haplorthox), Soil 2 (Typic Haplorthox), and Soil 3 (Typic Quartzipsamment).

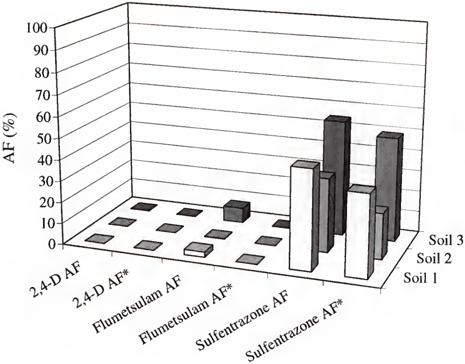

Figure 5-4. Overall pesticide attenuation factor values estimated by the original model (AF) and by the modified model (AF*) for Soil 1 (Quartzipsammentic Haplorthox), Soil 2 (Typic Haplorthox), and Soil 3 (Typic Quartzipsamment).

The pH-dependent AF values for flumetsulam were always much lower than values calculated by the original model (Figures 5-2). Therefore, the pH-independent model appears to overestimate this pesticide's leaching potential. The AF values for sulfentrazone calculated by the original and the modified models were similarly high for all three soils (Figures 5-3), despite the differences in K_d value. The long half-life of sulfentrazone mostly contributed to the similar high values of AF for the three different soils.

Overall AF values showed large differences for sulfentrazone when calculated by the original and by the modified model (Figure 5-4), owing to its high AF value for each

layer. Thus, the original AF model would seem to overestimate the leaching potential for sulfentrazone, as well as for flumetsulam for these soil conditions.

The pesticide sorption effect on degradation rate was not considered in this study. However, Ogram *et al.* (1985) suggested that microbial degradation of 2,4-D occurrs only in the solution phase, and not when the pesticide is sorbed. Fontaine *et al.* (1991) reported that the degradation rate of flumetsulam was faster in soils with lower sorption capacities. If a general suppressive effect of sorption on degradation was recognized, an increase in pesticide AF values estimated by the modified model would be expected when pH diminishes and sorption consequently increases.

Thus, greater sorption (as predicted by the pH-dependent model developed in this study) might lead to somewhat longer persistence of the pesticides in soils. This is of interest because (a) it provides still another means of testing both the sorption-prediction model and the "nondegraded-if-sorbed" theory; and (b) it also provides some interesting opportunities for decision-makers, based on decreased mobility vs. increased persistence of a given pesticide.

CHAPTER 6
SUMMARY AND CONCLUSIONS

A model of acidic pesticide sorption in soils was developed considering initially a combination of a strongly acidic pesticide and a variable-charge soil with high clay content. Model development was based on theoretical modeling and experimental data.

At low pH levels where acidic pesticides exist largely in neutral form, the soil sorbed much more 2,4-D than at high pH levels, where the pesticide is mostly in anionic form. Sorption of the acidic form is expected to decrease with increasing pH, because the net negative charge on the soil minerals increases and yet sorption continues to decrease, suggesting that ion-pair formation effects are negligible.

The contribution of 2,4-D anionic-form sorption was small when compared with its overall sorption for the soils initially studied. The role played by variable-charge minerals is expected to diminish in the presence of organic matter, even in soils with organic matter content of only 0.1%. Thus, the anionic-sorption contribution was not taken into account in the additional modeling work, and other data sets used in this study were not limited to variable-charge soils.

Dissociation of 2,4-D was not sufficient to explain the variation in K_d as a function of pH, and the accessibility of soil organic functional groups able to interact with the pesticide (conformational changes), as a function of organic matter dissociation, was proposed to explain the observed differences in sorption. Hydrophobicity of the neutral

form of the pesticide does not vary largely at low pH levels, and protonation of organic matter at very low pH does not appear to make it more hydrophobic.

Experimental 2,4-D sorption data adequately fit the model presented, and the model explained a majority of the variation observed in the experimental data set. The analysis made for 2,4-D was also applied to other acidic pesticides. The model presented was also able to estimate K_{oc} values for flumetsulam and sulfentrazone, as a function of pH in several soils. It is apparent that anionic-form sorption has been overvalued, and the overall effect of organic matter dissociation because of pH changes has been overlooked in published models for estimating the sorption of acidic compounds.

In addition, incorporating the developed sorption model made possible the improvement of an existing pesticide transport model. The pH-dependent K_d values estimated for all three pesticides were observed to always be higher than pH-independent K_d values calculated using average K_{oc} data, and therefore the original AF model for flumetsulam and sulfentrazone overestimated the overall leaching potential for the soils studied.

The modeling work for acidic pesticides made in this study is applicable to either tropical or temperate soils and can potentially be extended to nonionizable compounds. Further research on sorption modeling for basic compounds is needed and recommended.

APPENDIX

Table A-1. Properties of soils used in the flumetsulam sorption experiment by Fontaine *et al.* (1991).

Soil		Initial pH_{H_2O}	OC (%)
Soil 1	Typic Argiudoll	5.9	2.2
Soil 2	Typic Hapludult	6.4	0.6
Soil 3	Udic Haploboroll	6.8	3.1
Soil 4	Typic Haplaquoll	7.1	4.2

Table A-2. Properties of soils used in the sulfentrazone sorption experiment by Grey *et al.* (1997).

Soil		Clay (%)	O.M. (%)	Initial pH	Mineralogy(1)
Soil 1	Typic Unifluvent	6	1.0	6.3	K>V
Soil 2	Rhodic Paleudult	35	1.2	5.4	K>V≈S
Soil 3	Aeric Ochraqualf	30	3.1	6.7	K=S
Soil 4	Typic Rhodudult	30	2.8	5.8	K>>V>Gi

(1)Predominant minerals: K = kaolinite, V = vermiculite, S = smectite, Gi = gibbsite.

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BIOGRAPHICAL SKETCH

Claudio Spadotto was born in Botucatu, São Paulo State, Brazil, in 1962. He received a B.S. degree from the College of Agriculture at São Paulo State University in 1984, and an M.S. degree in Agronomy in 1990 at the same university.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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